

1.111.554



PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Process for producing Photographic Coloured Images and Colour Couplers for use therein

We, SOCIETA PER AZIONI FERRANIA, an Italian Body Corporate of Milan, Corso Matteotti 12, Italy, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

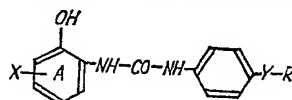
This invention relates to the production of colour photographic blue-green images by chromogenic development and to colour couplers of use in the process.

The use of alpha-naphtholic and phenolic colour couplers substituted in the 2- or 3-position to the —OH group, generally by carbonamido, acylamino, sulphonamido, or sulphonacylamido groups, to produce blue-green images by the chromogenic development of silver halide emulsions is known. The naphtholic compounds have been preferred inasmuch as the phenolic couplers form, by chromogenic development, dyes which are not very light stable. Moreover, photographic materials containing such dyes, when developed, and particularly copies on paper, have the disadvantage that they tend to yellow on exposure to daylight with the passage of time. This is due to the presence of residual colour coupler.

DAS 1,193,144 describes, as cyan couplers, 2-ureido-phenols which do not suffer from these disadvantages but the dyes derived therefrom through chromogenic development exhibit an absorption maximum at too low a wavelength. This maximum, in the dyes derived from couplers incorporated in a silver halide emulsion, is in general between 610 and 640 mμ with peaks up to 645 mμ so that the couplers are practically useless for the production of colour photographic images.

It has now been found that blue-green images having good characteristics can be produced by using, as colour coupling agents, certain substituted 2-ureido-phenol compounds.

In one aspect therefore the present invention provides compounds of the formula:



wherein X represents a hydrogen atom or one or more halogen atom or methyl or sulphonio group substituted in the 4-, 5- or 6-position of the benzene nucleus A, Y represents a group —NH—CO—, —CO—NH—, —NH—SO₂— or —SO₂NH— and R represents a hydrogen atom or an alkyl or aryl group which may be substituted by one or more solubilising group and/or one or more linear or branched alkyl group.

Colour photographic images may be produced in accordance with the invention by developing chromogenically a silver halide emulsion layer containing a developable latent image with a chromogenic developer in the presence of, as colour coupling agent, a 2-ureido-phenol compound of the invention. Preferably the chromogenic developer is N,N-diethyl-p-phenylene diamine. The products of the reaction of the colour coupling agents and the oxidation products of the developer are blue-green dyes which are light-stable and which display an absorption curve with a maximum centred in the spectral zone which is required for most of the colour materials obtained using the trichromatic subtractive process.

[Price 4s. 6d.]

In a further aspect the invention provides a photographic material comprising a silver halide emulsion layer containing, as colour coupling agent, a 2-ureido-phenol compound of the present invention.

In column I of the following Table there are set forth by way of comparison couplers which are within the general formula of DAS 1,163,144 and in column II couplers within the general formula of the compounds of the present invention. The Table also gives the absorption maximum of the dye derived from each coupler by chromogenic development.

TABLE

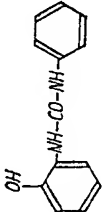
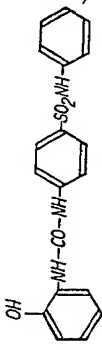
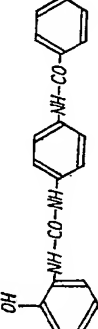
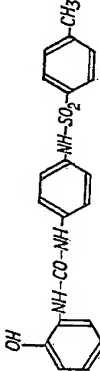
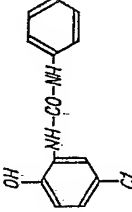
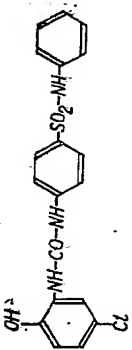
No.	Column I	Max. absorb. $m\mu$	No.	Column II	Max. absorb. $m\mu$
1		650	I		668
			II		657
			III		662
2		630	IV		680

TABLE (Continued)

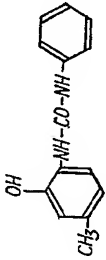
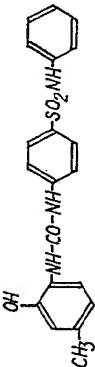
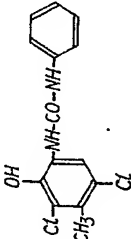
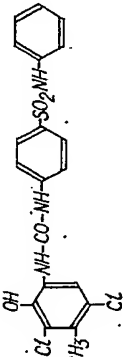
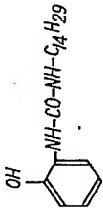
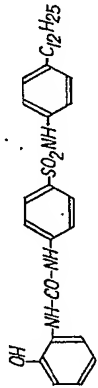
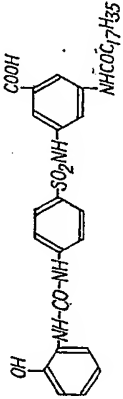
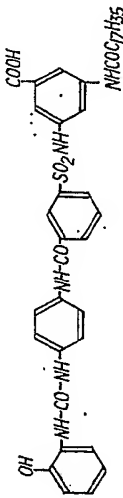
No.	Column I	Max. absorb. $m\mu$	No.	Column II	Max. absorb. $m\mu$
3		640	V		655
4		672	VI		695
5		627	VII		667
			VIII		655
			IX		655

TABLE (Continued)

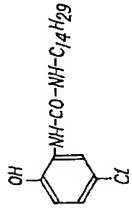
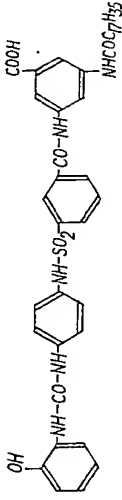
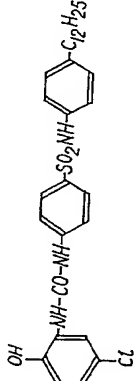
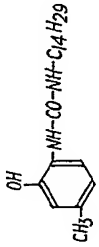
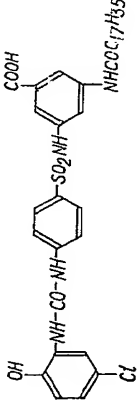
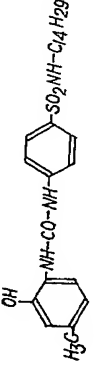
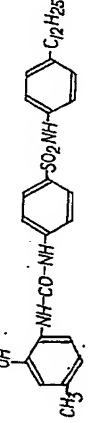
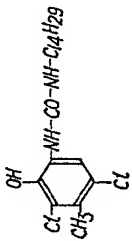
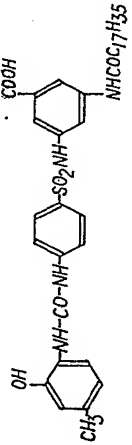
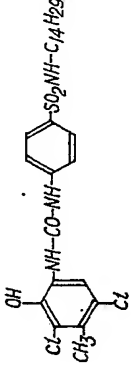
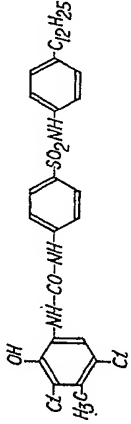
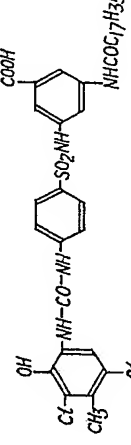
No.	Column I	Max. absorb. m μ	No.	Column II	Max. absorb. m μ
6		630	X		652
			XI		688
7		618	XII		658
			XIII		648
			XIV		655

TABLE (Continued)

No.	Column I	Max. absorb. $m\mu$	No.	Column II	Max. absorb. $m\mu$
8	 <chem>Cc1cc(Cl)cc(NC(=O)N)c1O</chem>	608	XV	 <chem>Cc1cc(Cl)cc(NC(=O)Nc2ccc(S(=O)(=O)Nc3ccc(C(=O)O)cc3)cc2)c1O</chem>	640
			XVI	 <chem>Cc1cc(Cl)cc(NC(=O)Nc2ccc(S(=O)(=O)Nc3ccc(C(=O)O)cc3)cc2)c1O</chem>	656
			XVII	 <chem>Cc1cc(Cl)cc(NC(=O)Nc2ccc(S(=O)(=O)Nc3ccc(C(=O)O)cc3)cc2)c1O</chem>	668
			XVIII	 <chem>Cc1cc(Cl)cc(NC(=O)Nc2ccc(S(=O)(=O)Nc3ccc(C(=O)O)cc3)cc2)c1O</chem>	652

The Couplers I to XVIII listed in the Table were prepared as follows:

Coupler I

- 5 10.9 g of *o*-aminophenol were dissolved in dioxane and the solution was heated. 21.75 g of *p*-chlorosulphophenylisocyanate were added to the hot solution which was then refluxed for one hour. The solution formed was poured into a boiling solution of 7.45 g of aniline in dioxane and pyridine. After purification from ethanol-water 36 g of the Coupler I, which melted at 203—205°C., were separated. 5

Coupler II

- 10 2.43 g. of 2(*p*-aminophenyl) ureidophenol were suspended in dioxane and pyridine and added to 1.4 g of benzoylchloride. The mixture was refluxed and the solution was then decanted to free it from gums and poured into dilute hydrochloric acid. 3.5 g of impure Coupler II were obtained and these were subsequently purified, using aqueous alcohol, to obtain a product which sintered at 200°C. 10

- 15 The 2(*p*-aminophenyl) ureidophenol used as starting material was obtained by the reduction of 2(*p*'-nitrophenyl) ureidophenol. This was itself obtained by dissolving 10.9 g of *o*-aminophenol in dioxane, adding 16.4 g of *p*-nitrophenyl-isocyanate in dioxane solution to the solution at 15—16°C. and purifying the product with aqueous ethanol to give 25 g of a product melting at 213—215°C. 15

Coupler III

- 20 2.43 g of 2(*p*-aminophenyl)ureidophenol were dissolved in pyridine. 1.9 g of *p*-toluenesulphonyl chloride were added to the solution. The mixture was allowed to reflux for one hour and then it was poured into dilute hydrochloric acid. 3.6 g of impure Coupler III were obtained. They were subsequently purified from aqueous ethanol to give a product melting at 183—186°C. 20

Coupler IV

- 25 This was prepared in the same manner as Coupler I except that 2-amino-4-chlorophenol was used instead of *o*-aminophenol. The product melted at 205—207°C. 25

Coupler V

- 30 This was prepared in the same manner as Coupler I except that 2-amino-5-methylphenol was used instead of *o*-aminophenol. After purification there was obtained a product melting at 192—193°C. 30

Coupler VI

- 35 This was prepared in the same manner as Coupler I except that 2-amino-5-methyl-4,6-dichlorophenol was used instead of *o*-aminophenol. The product obtained melted at 232—234°C. 35

Coupler VII

- 40 10.9 g of *o*-aminophenol were dissolved in dioxane. 21.75 g of *p*-chlorosulphophenylisocyanate were added to the hot solution which was then refluxed for one hour. The solution was poured into a boiling solution of 24.83 g of *p*-dodecylaniline in dioxane and pyridine. 50 g of product were separated, which after suspension in benzene, melted at 141—144°C. 40

Coupler VIII

- 45 This was prepared in the same manner as Coupler VII except that 3-amino-5-stearoylaminobenzoic acid was used instead of *p*-dodecylaniline. 63 g of a product crystallized from acetonitrile and melted at 154—158°C. 45

Coupler IX

- 50 2.43 g of 2(*p*-aminophenyl) ureidophenol were suspended in dioxane. 2.39 g of *m*-chlorosulphobenzoyl chloride were added and the mixture was refluxed for one hour. The solution formed was poured into a boiling solution of 3.76 g of 3-amino-5-stearoylamino-benzoic acid in dioxane and pyridine. After purification with acetone and then with petroleum ether, 7.6 g of product were obtained melting at 158—162°C. 50

Coupler X

- 2.43 g of 2(*p*-aminophenyl) ureidophenol were suspended in dioxane and pyridine. 6.21 g of 3-chlorosulpho-(3'-carboxy-5'-stearoylamino)benzanilide were added at room

temperature. The mixture was refluxed for one hour in order to obtain a solution which was poured into dilute hydrochloric acid. 7.6 g of product were purified with acetone and petroleum ether and melted at 160—164°C.

- 5 The 3-chlorosulpho-(3'-carboxy-5'-stearoylamino)benzanilide was prepared by heating up to boiling a solution of 3-amino-5-stearoylaminobenzoic acid in acetone, adding sulphobenzodichloride, and allowing to reflux for one hour. After washing with acetone a product was obtained which melted at 198—200°C. 5

Coupler XI

- 10 This was prepared in the same maner as Coupler VII except that 2-amino-4-chlorophenol was used instead of *o*-aminophenol. The product obtained melted at 168—169°C. 10

Coupler XII

- 15 This was prepared in the same manner as Coupler VIII except that 2-amino-4-chlorophenol was used instead of *o*-aminophenol. The product obtained, after purification from ethanol and acetonitrile, melted at 174—175°C. 15

Coupler XIII

- 20 12.3 g of 2-amino-5-methylphenol were dissolved in dioxane. 21.7 g of *p*-chlorosulphophenyl-isocyanate were added to the warm solution which was then refluxed for one hour. The solution formed was poured into a boiling solution of 20.2 g of tetradecylamine in dioxane and pyridine. 50 g of product were separated, which after crystallisation from acetonitrile, melted at 148—152°C. 20

Coupler XIV

- 25 This was prepared in the same manner as Coupler VII except that 2-amino-5-methylphenol was used instead of *o*-aminophenol. After purification with benzene and petroleum ether a product was obtained which melted at 122—124°C. 25

Coupler XV

This was prepared in the same manner as Coupler VIII except that 2-amino-5-methylphenol was used instead of *o*-aminophenol. The product obtained melted at 162—164°C.

- 30 **Coupler XVI** 30

This was prepared in the same manner as Coupler XIII except that 2-amino-5-methyl-4,6-dichlorophenol was used instead of *o*-aminophenol. The product obtained melted at 126—130°C.

Coupler XVII

- 35 This was prepared in the same manner as Coupler VII except that 5-methyl-4,6-dichlorophenol was used instead of *o*-aminophenol. After crystallization from acetonitrile a product was obtained which melted at 193—195°C. 35

Coupler XVIII

- 40 This was prepared in the same manner as Coupler VIII except that 2-amino-5-methyl-4,6-dichlorophenol was used instead of *o*-aminophenol. The product obtained melted at 147—167°C. 40

All of the above described Couplers I to XVIII may be used to produce colour photographic images by chromogenic development. This is illustrated by the following Examples.

EXAMPLE 1

- 45 A sample of photographic material containing a silver halide emulsion was exposed and then developed in a chromogenic developer having the following composition: 45

	Anhydrous sodium carbonate	20 g	
	Anhydrous sodium sulphite	0.5 g	
	N,N-diethyl- <i>p</i> -phenylenediamine sulphate	1 g	
50	Coupler I	1 g	50
	Water to make	1000 ml	

The developed material was washed, then treated in a bleaching bath, washed, fixed, washed again and dried. A blue-green coloured image was thus obtained, through the formation of a dye, and had an absorption maximum at 668 m μ .

- 55 When Coupler I in the chomogenic developer is replaced by Couplers II, III, 55

IV, V and VI, cyan colour images are obtained through the formation of dyes showing an absorption maximum at 657, 662, 680, 655 and 695 m μ , respectively.

By the same process but using the compounds 1, 2, 3 and 4 shown in Column I of the Table, dyes are obtained with an absorption maximum at 650, 630, 640 and 670 m μ , respectively.

EXAMPLE 2

10 g of Coupler VIII were dissolved in 20 ml of methanol, 15 ml of 2N NaOH solution and 250 ml of water. This solution was added, in accordance with a conventional technique, to 1 kg of silver halide photographic emulsion which was then coated on a suitable base. The photosensitive material thus obtained was exposed and then developed with an N,N-diethyl-*p*-phenylenediamine chromogenic developer. After bleaching and fixing, a blue-green dye image having an absorption maximum at 655 m μ was obtained in the exposed areas.

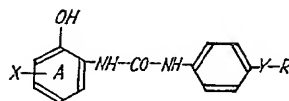
Couplers VII, IX, X, XI, XII, XIII, XIV, XV, XVI, XVII and XVIII may be employed similarly to give dyes with an absorption maximum at 667, 655, 652, 668, 658, 648, 655, 640, 656, 668 and 652 m μ respectively. Compounds 5, 6, 7 and 8 shown in Column I of the Table when used similarly provide dyes with an absorption maximum at 627, 630, 618, 608 m μ , respectively.

EXAMPLE 3

Couplers VII, XI, XIII and XVI may also be employed in the following way. 10 g of the coupler were dissolved at 50°C. in 20 ml of dibutyl phthalate and 60 ml of ethyl acetate. This solution was added to 200 ml of a 4% solution of inert gelatine containing also 10 ml of a 10% solution of "Tergitol" 4 ("Tergitol" is a Registered Trade Mark for a sodium tetradecyl-sulphonate preparation produced by Union Carbide Corporation). The mixture was passed to a suitable homogenizer and the dispersion obtained was added to 1 kg of a silver halide photographic emulsion which was then coated on a suitable base. The photosensitive material thus obtained was exposed and then developed with an N,N-diethyl-*p*-phenylenediamine chromogenic developer. After bleaching and fixing a blue-green image was obtained in the exposed areas due to the formation of dyes each having an absorption maximum at the wavelengths already listed in Example 2.

WHAT WE CLAIM IS:—

1. A 2-ureidophenol compound of the formula:



wherein X represents a hydrogen atom or one or more halogen atom or methyl or sulphonic group substituted in the 4-, 5- or 6-position of the benzene nucleus A, Y represents a group —NH—CO—, —CO—NH—, —NH—SO₂— or —SO₂NH— and R represents a hydrogen atom or an alkyl or aryl group which may be substituted by one or more solubilising group and/or one or more linear or branched alkyl group.

2. The compounds represented by the formulae I to XVIII given hereinbefore.

3. A 2-ureidophenol compound as claimed in claim 1 substantially as hereinbefore described.

4. A process for the production of a colour photographic image which comprises developing chromogenically a silver halide emulsion layer containing a developable latent image with a chromogenic developer in the presence of, as colour coupling agent, a 2-ureidophenol compound as claimed in any one of claims 1 to 3.

5. Process according to claim 4, wherein the chromogenic developer is N,N-diethyl-*p*-phenylene diamine.

6. Process according to claim 4 for the production of a colour photographic image substantially as described in any of the Examples.

7. Colour photographic images whenever produced by the process claimed in claim 4, 5 or 6.

8. A photographic material comprising a silver halide emulsion layer containing as colour coupling agent, a 2-ureidophenol compound as claimed in any one of claims 1 to 3.

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